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ORIGINAL PAPER

Design, synthesis, characterization and fluorescence property evaluation of dehydroacetic acid-based chalcones

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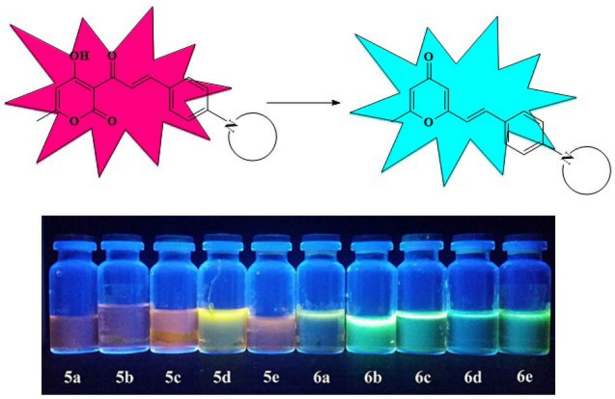
Abstract

In this study, we decided to synthesize some new chalcone-type dyes derived from dehydroacetic acid (DHA) by the condensation of 4-amino-substituted benzaldehyde with DHA under the base-catalyzed condition and investigate their ability for rearrangement in acidic condition. For this purpose, initially we prepared the 4-aminobenzaldehyde derivatives via nucleophilic aromatic substitution reaction of 4-fluorobenzaldehyde with variety of amines in the presence of K_2CO_3 as base in DMF. The Knoevenagel condensation of DHA with 4-aminobenzaldehyde derivatives results in the desired compounds. In continuation, Fries rearrangement applied on DHA-chalcone compounds results in characterization of new pyranilidene-type derivatives. The optical responses of new dyes containing UV–Vis absorption and fluorescence spectroscopy were measured in dichloromethane (ET = 40 kcal/mol). Pyranilidene derivatives show low λ_{max} values in comparison with chalcones, and molecule with strong dipole, in polar solvents, shows the bathochromic shift due to more stabilization of excited state in compared with ground state of molecule. Large stocks shifts were obtained for synthesized compounds.

Graphic abstract



Keywords Dehydroacetic acid · Chalcone · 4-Amino-substituted benzaldehyde · Pyran

Introduction

The heterocyclic compounds, particularly oxygen-containing heterocycles, are challenging models for a large number of usages in organic chemistry. 3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one is one of the important oxygen-containing heterocyclic compounds; it is commonly known as dehydroacetic acid (DHA). DHA and the products derived from it found wide application in various physiological and

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synthetic areas as well as pharmaceutical, cosmetic and food industries [1–3].

DHA with four active sites is a susceptible molecule for nucleophilic and electrophilic reactions. DHA can react with different aldehydes and produce variety of chalcones [4, 5]. The chalcones are important conjugated systems which are used as intermediates to synthesize various applicable derivatives. Representative examples of natural structures with chalcone units are illustrated in Fig. 1.

Conjugated systems are potential privileged compounds that have been known due to their excellent photo-physical and optical properties. These type compounds have been vastly explored in lasers, fluorogenic probes, pigments, solar cells, nonlinear optical materials, etc. [6–8].

Outstanding feature of DHA and its derivatives is their ability to rearrangement to 4*H*-pyran-4-one derivatives. Research work in our laboratory has been recently concerned with the reaction of 4*H*-pyran derivatives with various aromatic aldehydes in order to conjugated compounds with modified optical properties [9–12]. In this research, we report the synthesis of some new chalcone derivatives with DHA core via Knoevenagel condensation of DHA with amine-substituted aldehydes, followed by rearrangement to 4*H*-pyran derivatives. In addition, their UV–Vis absorption and fluorescence emission properties were studied.

Experimental

General

Commercial compounds were used without further purification. Column chromatography was performed using SiO2 (60 Å, 230–400 mesh, particle size 0.040–0.063 mm) at 25 °C. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at 25 °C using $CDCl_3$ as solvent, with chemical shifts measured in ppm and referenced to the residual solvent as follows: $CHCl_3 = 7.26$ ppm (^{1}H), 76.0 ppm (^{13}C). FT-IR spectral data are reported as wave numbers (cm^{-1}). Elemental analyses were carried out with an Elementar Vario EL III instrument. The mass spectra are operated at 70 eV by Agilent (5975C VL) instrument; the most important peaks are reported in *m*/*z* units with M^+ as the molecular ion and with the corresponding intensities in %. The electronic absorption spectra were obtained using SPECORD 250 Analytik Jena UV/Vis spectrophotometer; fluorescence emission spectra were measured on an Edinburgh FLS 920 fluorometer (UK). Melting points were determined on a MEL-TEMP model 1202D and are uncorrected.

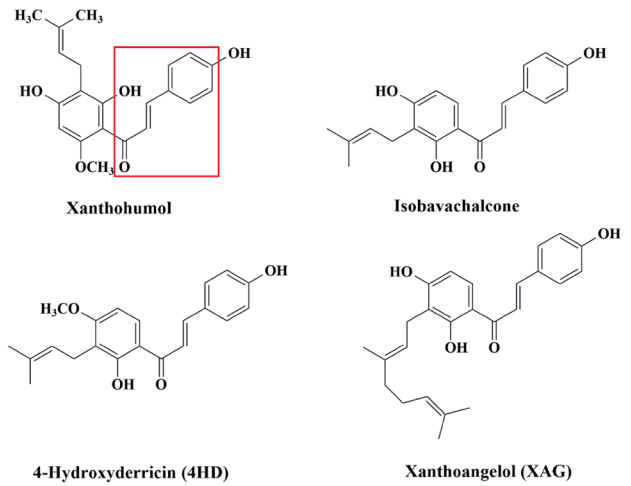


Fig. 1 Representative examples of chalcone units in natural structures

General procedure for the synthesis of 4-amino-substituted benzaldehyde (3a–e)

A mixture of 4-fluorobenzaldehyde (**1**) (0.25 g, 2 mmol), appropriate amines (**2a**–**e**) (3 mmol) and anhydrous potassium carbonate (0.4 g) was stirred in DMF (5 mL) for 24 h at 80 °C. The mixture was concentrated under low pressure and left to cool. The mixture was then poured into ice water and left overnight. The formed solid was filtered, washed with water and crystallized with methanol to yield compounds **3a**–**e** [13].

General procedure for the synthesis of chalcone DHA derivatives (5a–e)

In a round bottom flask equipped with a magnetic stir bar, reflux condenser and a Soxhlet condenser filled with molecular sieves, DHA (**4**, 0.168 g, 1 mmol), 1 mmol of appropriate amino benzaldehyde **3a**–**e** and catalytic amount of piperidine (8.5 mg, 0.1 mmol) were refluxed in dry toluene for 24 h. After complete reaction, toluene was removed under reduced pressure and residue was dissolved in CH_2Cl_2 and washed with water. Combined organic layer was dried over the anhydrous Na_2SO_4, and the solvent was removed in atmospheric pressure. Obtained crude solid was purified by recrystallization from EtOH.

3-[3-(4-Dimethylamino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (5a)

Using 0.149 g of 4-(dimethylamino)benzaldehyde, 0.268 g (0.89 mmol) of orange solid was obtained in 89% yield. m.p: 220–222 °C; FT-IR (KBr, cm^{-1}): 3447 (–OH), 2924 (Aromatic, –CH), 2854 (Aliphatic, –CH), 1695 (C=O), 1241 (C–N); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.36 (s, 1H, OH), 8.18–8.14 (dd, 1H, J = 16 Hz, =CH), 7.99–7.95 (dd, 1H, J = 16 Hz, =CH), 7.67–7.64 (d, 2H, J = 12 Hz, Ar), 6.99–6.96 (d, 2H, J = 12 Hz, Ar), 5.93 (s, 1H, Pyran), 2.66 (s,

3H, –CH_3), 2.27–2.26 (s, 6H, N-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 183.70, 174.50, 165.42, 165.05, 149.70, 141.27, 128.94, 125.63, 125.42, 111.30, 103.40, 102.14, 46.75, 20.83; MS (70 eV): *m*/*z* (%): 299.12 (100) [M^+]. Elemental analysis: calcd. for $C_{17}H_{17}NO_4$ (%): C 68.22, H 5.72, N 4.68; found (%): C 67.93, H 5.71, N 4.69.

3-[3-(4-Pyrrolidino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (5b)

Using 0.175 g of 4-(pyrrolidino)benzaldehyde, 0.313 g (0.96 mmol) of brown solid was obtained in 96% yield. m.p: 174–176 °C; FT-IR (KBr, cm^{-1}): 3450 (–OH), 3114 (Aromatic, –CH), 2923 (Aliphatic, –CH), 1696 (C=O), 1324 (C–N); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.71 (s, 1H, OH), 8.11–8.07 (dd, 1H, *J* = 16 Hz, =CH), 8.03–7.99 (dd, 1H, *J* = 16 Hz, =CH), 7.61–7.59 (d, 2H, *J* = 12 Hz, Ar), 6.57–6.54 (d, 2H, *J* = 8 Hz, Ar), 5.90 (s, 1H, Pyran), 3.40–3.37 (t, 4H, N-CH_2), 2.24 (s, 3H, –CH_3), 2.06–2.02 (m, 4H, –CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 189.98, 183.00, 166.17, 149.27, 147.68, 141.20, 131.06, 125.18, 121.38, 114.63, 111.00, 102.28, 46.75, 24.40, 19.47; MS (70 eV): *m*/*z* (%): 325.13 (100) [M^+]. Elemental analysis: calcd. for $C_{19}H_{19}NO_4$ (%): C 70.14, H 5.89, N 4.31; found (%): C 70.08, H 5.88, N 4.32.

3-[3-(4-Piperidino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (5c)

Using 0.189 g of 4-(piperidino)benzaldehyde, 0.308 g (0.91 mmol) of dark brown solid was obtained in 91% yield. m.p: 178–180 °C; FT-IR (KBr, cm^{-1}): 3415 (–OH), 3086 (Aromatic, –CH), 2931 (Aliphatic, –CH), 1711 (C=O), 1236 (C–N); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.57 (s, 1H, OH), 8.15–8.11 (dd, 1H, *J* = 16 Hz, =CH), 7.99–7.95 (dd, 1H, *J* = 16 Hz, =CH), 7.60–7.58 (d, 2H, *J* = 8 Hz, Ar), 6.87–6.85 (d, 2H, *J* = 8 Hz, Ar), 5.91 (s, 1H, Pyran), 3.38–3.37 (t, 4H, N-CH_2), 2.24 (s, 3H, –CH_3), 1.69 (m, 6H, –CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 188.61, 179.61, 165.88, 147.36, 146.95, 141.51, 129.15, 123.45, 115.75, 113.15, 101.35, 99.50, 45.88, 23.53, 19.70, 13.24; MS (70 eV): *m*/*z* (%): 339.15 (100) [M^+]. Elemental analysis: calcd. for $C_{20}H_{21}NO_4$ (%): C 70.78, H 6.24, N 4.13; found (%): C 70.75, H 6.25, N 4.14.

3-[3-(*N*-Methylpiperazino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (5d)

Using 0.204 g of 4-(*N*-methylpiperazino)benzaldehyde, 0.336 g (0.95 mmol) of dark brown solid was obtained in 95% yield. m.p: 195–197 °C; FT-IR (KBr, cm^{-1}): 3407 (–OH), 2933 (Aromatic, –CH), 2854 (Aliphatic, –CH), 1698 (C=O), 1243 (C–N); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.43 (s, 1H, OH), 8.17–8.13 (dd, 1H, *J* = 16 Hz, =CH), 7.98–7.94 (dd, 1H, *J* = 16 Hz, =CH),7.62–7.60 (d, 2H, *J* = 8 Hz, Ar), 6.89–6.87 (d, 2H, *J* = 8 Hz, Ar), 5.92 (s, 1H, Pyran), 3.41–3.37 (3, 4H, N-CH_2), 2.59–2.58 (3, 4H, N-CH_2), 2.37 (s, 3H, N-CH_3), 2.25 (s, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 183.08, 174.83, 166.33, 164.50, 142.23, 129.15, 125.87, 124.32, 113.33, 104.44, 102.10, 54.83, 46.60, 25.50, 20.58; MS (70 eV): *m*/*z* (%): 354.16 (100) [M^+]. Elemental analysis: calcd. for $C_{20}H_{22}N_2O_4$ (%): C 67.78, H 6.26, N 7.90; found (%): C 67.75, H 6.27, N 7.91.

3-[3-(4-Morpholino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (5e)

Using 0.191 g of 4-(morpholino)benzaldehyde, 0.296 g (0.87 mmol) of dark brown orange was obtained in 87% yield. m.p: 241–242 °C; FT-IR (KBr, cm^{-1}): 3448 (–OH), 3115 (Aromatic, –CH), 2924 (Aliphatic, –CH), 1712 (C=O), 1264 (C–N); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.33 (s, 1H, OH), 8.20–8.16 (dd, 1H, *J* = 16 Hz, =CH), 7.98–7.94 (dd, 1H, *J* = 16 Hz, =CH), 7.65–7.63 (d, 2H, *J* = 8 Hz, Ar), 6.98–6.96 (d, 2H, *J* = 8 Hz, Ar), 5.94 (s, 1H, Pyran), 3.90 (t, 4H, CH_2), 3.32 (t, 4H, –CH_2), 2.27 (s, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 180.24, 170.28, 165.48, 160.35, 147.68, 125.57, 125.20, 123.25, 110.45, 103.17, 101.10, 65.30, 46.75, 18.70; MS (70 eV): *m*/*z* (%): 341.13 (100) [M^+]. Elemental analysis: calcd. for $C_{19}H_{19}NO_5$ (%): C 66.85, H 5.61, N 4.10; found (%): C 66.83, H 6.62, N 4.11.

General procedure for the Fries rearrangement

A mixture of 1 mmol chalcone DHA derivatives **5a**–**e** in acetic acid (5 mL) and concentrated hydrochloric acid (5 mL) was heated at 110 °C for 5 h. To cold reaction mixture, 5 mL of distilled water was added and decomposed with cold sodium hydroxide solution (10%). Obtained solid was filtered and washed with water. The crude products were purified by recrystallization from EtOH.

2-[(4-Dimethylamino)styryl]-6-methyl-4*H*-pyran-4-one (6a)

Using 0.299 g of **5a**, 0.234 g (0.92 mmol) of orange solid was obtained in 92% yield. m.p: 185–187 °C; FT-IR (KBr, cm^{-1}): 3062 (Aromatic, –CH), 2960 (Aliphatic, –CH), 1704 (C=O), 1233 (C–N), 1118 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.57–7.53 (d, 2H, *J* = 8 Hz, Ar), 7.32–7.28 (dd, 1H, *J* = 16 Hz, =CH), 6.95–6.93 (d, 2H, *J* = 8 Hz, Ar), 6.84–6.80 (dd, 1H, *J* = 16 Hz, =CH), 6.17 (s, 1H, Pyran), 6.10 (s, 1H, Pyran), 3.26 (s, 6H, N-CH_3), 2.26 (s, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K):

δ [ppm] = 188.29, 167.16, 162.77, 152.82, 137.27, 127.70, 123.27, 117.52, 114.32, 112.71, 110.32, 40.12, 19.27; MS (70 eV): *m*/*z* (%): 255.13 (100) [M^+]. Elemental analysis: calcd. for $C_{16}H_{17}NO_2$ (%): C 75.27, H 6.71, N 5.49; found (%): C 75.25, H 6.72, N 5.50.

2-[4-(Pyrrolidin-1-yl)styryl]-6-methyl-4*H*-pyran-4-one (6b)

Using 0.325 g of **5b**, 0.247 g (0.88 mmol) of light orange solid was obtained in 88% yield. m.p: 126–128 °C; FT-IR (KBr, cm^{-1}): 3112 (Aromatic, –CH), 2923 (Aliphatic, –CH), 1652 (C=O), 1271 (C–N), 1031 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.74–7.71 (d, 2H, *J* = 8 Hz, Ar), 7.36–7.32 (dd, 1H, *J* = 16 Hz, =CH), 6.96–6.94 (d, 2H, *J* = 8 Hz, Ar), 6.90–6.86 (dd, 1H, *J* = 16 Hz, =CH), 6.22 (s, 1H, Pyran), 6.17 (s, 1H, Pyran), 3.42–3.20 (t, 4H, N-CH_2), 2.45–2.42 (m, 4H, –CH_2), 2.25 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 187.20, 168.50, 162.65, 152.70, 132.45, 130.23, 125.68, 120.12, 114.40, 112.28, 95.87, 53.80, 23.50, 20.49; MS (70 eV): *m*/*z* (%): 281.14 (100) [M^+]. Elemental analysis: calcd. for $C_{18}H_{19}NO_2$ (%): C 76.84, H 6.81, N 4.98; found (%): C 76.86, H 6.80, N 4.99.

2-[(4-(Piperidin-1-yl)styryl]-6-methyl-4*H*-pyran-4-one (6c)

Using 0.339 g of **5c**, 0.250 g (0.85 mmol) of brown solid was obtained in 85% yield. m.p: 135–139 °C; FT-IR (KBr, cm^{-1}): 3086 (Aromatic, –CH), 2960 (Aliphatic, –CH), 1711 (C=O), 1236 (C–N), 1120 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.43–7.41 (d, 2H, *J* = 8 Hz, Ar), 7.31–7.27 (dd, 1H, *J* = 16 Hz, =CH), 6.98–6.96 (d, 2H, *J* = 8 Hz, Ar), 6.51–6.47 (dd, 1H, *J* = 16 Hz, =CH), 6.14 (s, 1H, Pyran), 6.07 (s, 1H, Pyran), 3.28 (t, 4H, N-CH_2), 2.32 (s, 3H, CH_3), 1.71–1.63 (m, 6H, –CH_2),; ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 179.30, 165.10, 162.30, 155.80, 137.07, 126.90, 126.33, 116.02, 114.48, 114.35, 111.70, 47.05, 38.07, 20.43, 18.72; MS (70 eV): *m*/*z* (%): 295.16 (100) [M^+]. Elemental analysis: calcd. for $C_{19}H_{21}NO_2$ (%): C 77.26, H 7.17, N 4.74; found (%): C 77.24, H 7.16, N 4.75.

2-[4-(*N*-methylpiperazine-1-yl)styryl]-6-methyl-4*H*-pyran-4-one (6d)

Using 0.354 g of **5d**, 0.257 g (0.83 mmol) of yellow solid was obtained in 83% yield. m.p: 152–154 °C; FT-IR (KBr, cm^{-1}): 3039 (Aromatic, –CH), 2930 (Aliphatic, –CH), 1655 (C=O), 1242 (C–N), 1150 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.43–7.41 (d, 2H, *J* = 8 Hz, Ar), 7.30–7.26 (dd, 1H, *J* = 16 Hz, =CH), 6.89–6.87 (d, 2H, *J* = 8 Hz, Ar), 6.50–6.46 (dd, 1H, *J* = 16 Hz, =CH), 6.14 (s, 1H, Pyran), 6.05 (s, 1H, Pyran), 3.33 (t, 4H, N-CH_2), 2.69 (t, 4H, N-CH_2), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 181.30, 167.16, 162.58, 152.80, 134.15, 126.90, 114.40, 114.33, 113.32, 111.30, 47.43, 40.12, 39.91, 18.79; MS (70 eV): *m*/*z* (%): 310.17 (100) [M^+]. Elemental analysis: calcd. for $C_{19}H_{22}N_2O_2$ (%): C 73.52, H 7.14, N 9.03; found (%): C 73.55, H 7.15, N 9.02.

2-[4-(Morpholino)styryl]-6-methyl-4*H*-pyran-4-one (6e)

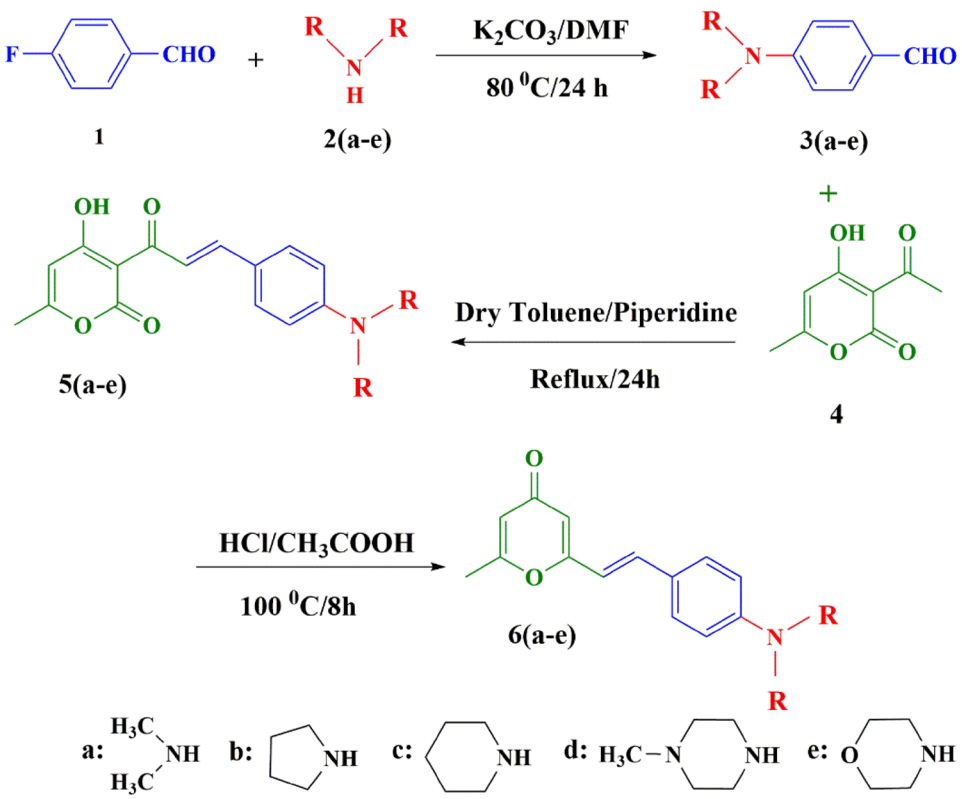
Using 0.341 g of **5e**, 0.285 g (0.96 mmol) of light orange solid was obtained in 96% yield. m.p: 192–194 °C; FT-IR (KBr, cm^{-1}): 3046 (Aromatic, –CH), 2953 (Aliphatic, –CH), 1706 (C=O), 1232 (C–N), 1116 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.54–7.51 (d, 2H, *J* = 8 Hz, Ar), 7.34–7.30 (dd, 1H, *J* = 16 Hz, =CH), 6.98–6.96 (d, 2H, *J* = 8 Hz, Ar), 6.86–6.84 (dd, 1H, *J* = 16 Hz, =CH), 6.19 (s, 1H, Pyran), 6.07 (s, 1H, Pyran), 3.72 (t, 4H, N-CH_2), 3.20 (t, 4H, O-CH_2), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 178.89, 165.16, 162.30, 151.80, 135.07, 128.90, 125.33, 116.02, 114.40, 113.32, 111.70, 65.96, 47.43, 19.27; MS (70 eV): *m*/*z* (%): 297.14 (100) [M^+]. Elemental analysis: calcd. for $C_{18}H_{19}NO_3$ (%): C 72.71, H 6.44, N 4.71; found (%): C 77.73, H 6.43, N 4.72.

Result and discussion

Chalcone derivatives are attractive candidates for linear and nonlinear optical applications. These types of compounds find unique potential for use in wide range of practical optic fields. Various methods were reported for preparation of chalcones in the literature. The most convenient procedure is involving the base-mediated condensation of aryl aldehyde with aryl methyl ketone. In order to preparation of DHA-based chalcones, we used Knoevenagel condensation of dehydroacetic acid as methyl ketone with 4-amino-substituted benzaldehyde. Firstly, benzaldehyde derivatives were prepared via nucleophilic aromatic substitution of secondary amines with 4-fluorobenzaldehyde in DMF and K_2CO_3 was employed as the base for the coupling reaction [13].

Obtained aldehydes were reacted with DHA under Knoevenagel condensation reaction condition (Scheme 1). As results that are obtained from experiments, dry toluene was chosen as solvent because we need higher temperature to complete the reaction. In the mild temperature which can be supplied with aldol condensation routine alcoholic solvents such as methanol and ethanol, the reaction was not complete. In addition, we used Soxhlet extractor filled with 4°A molecular sieves to remove the produced water during the reaction. Catalytic amount of piperidine was effective in progression of the reaction. In the literature, **5a** and **5e** were synthesized via complexion of DHA with BF_3 to increase the reactivity of 3-position acetyl group toward aldehydes, and hydrolysis of obtained complex in final step [14, 15]. In

Scheme 1 Synthesis of chalcone DHA derivatives (**5a**–**e**) and Fries rearrangement on them



comparison, our method is preferred due to less number of reaction steps and affordable used materials.

In continuation, we examined the Fries rearrangement in acidic condition for synthesized chalcone derivatives. Using acetic acid and hydrochloric acid in 100 °C for 8 h gives us the pyranilidene derivatives of relevant aldehydes. All molecular structures of the synthesized compounds were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopies and elemental analysis. Figure 2 depicts the ^{1}H NMR spectra of **5c** and **6c** as representative of chalcone derivative and its rearrangement products. Disappear of the largest chemical shift belongs to the alcoholic proton of

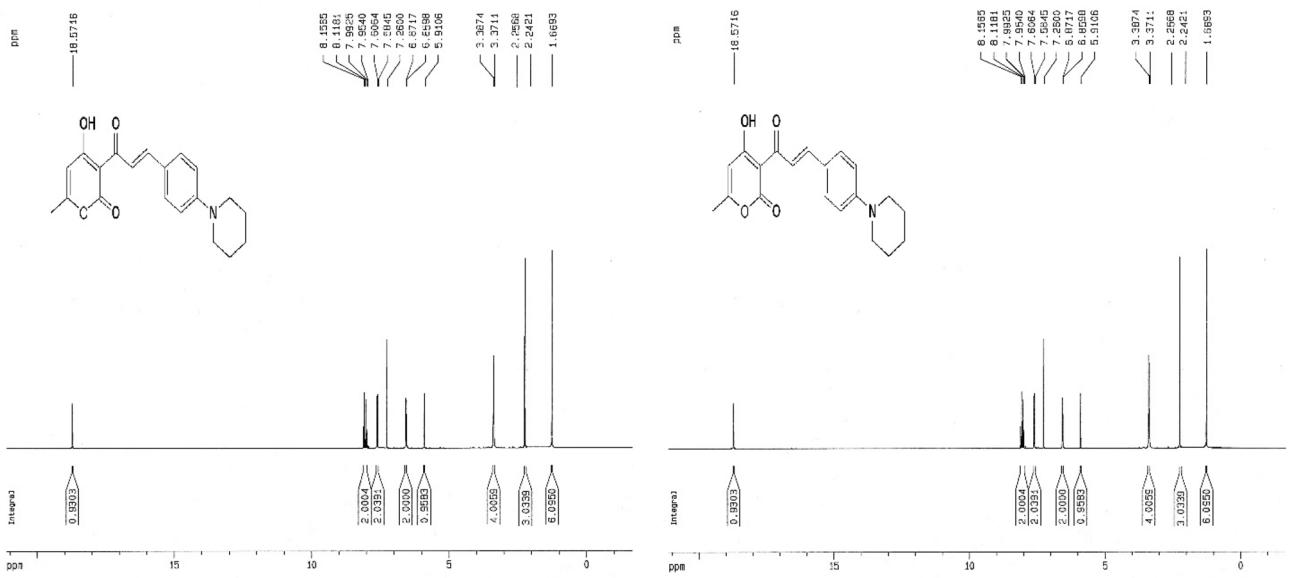


Fig. 2 ^{1}H NMR spectra of **5c** and **6c** as representative of chalcone derivatives and its rearrangement products

DHA in ^{1}H NMR spectra of **6c** is a confirmation that Fries rearrangement was performed.

Doublet signals in 7–8 ppm with coupling constant of 16 Hz in ^{1}H NMR spectra of **5c** related to exocyclic acrylic protons corresponding to all-*trans* geometry for synthesized chalcones and during Fries rearrangement, this geometry remains intact.

To evaluate the optical properties of synthesized compounds, we measured the electronic absorption and fluorescence spectra of chalcone and pyranilidene derivatives in dichloromethane. As can be seen from Fig. 3, the absorption spectra of target compounds exhibit a strong π–π* transition in the range of 443–491 for chalcone derivatives and 378–442 for pyranilidene-based compounds. The related descriptions are presented in Table 1.

Comparison between compounds series **5** and **6** shows the larger λ_{max} value for chalcone derivatives (**5a**–**e**) which exhibited smaller transition energies. We know compounds **5** and **6** shared same donor groups; thus, their transition energies can depend on molecular structure of chromophores. Dichloromethane is a polar solvent with ET = 40 kcal/mol; it is obvious that a molecule with strong dipole, in polar solvents, shows the bathochromic shift due to more stabilization of excited state in comparison with ground state of molecule. This phenomenon is in agreement with decrease in the transition energy.

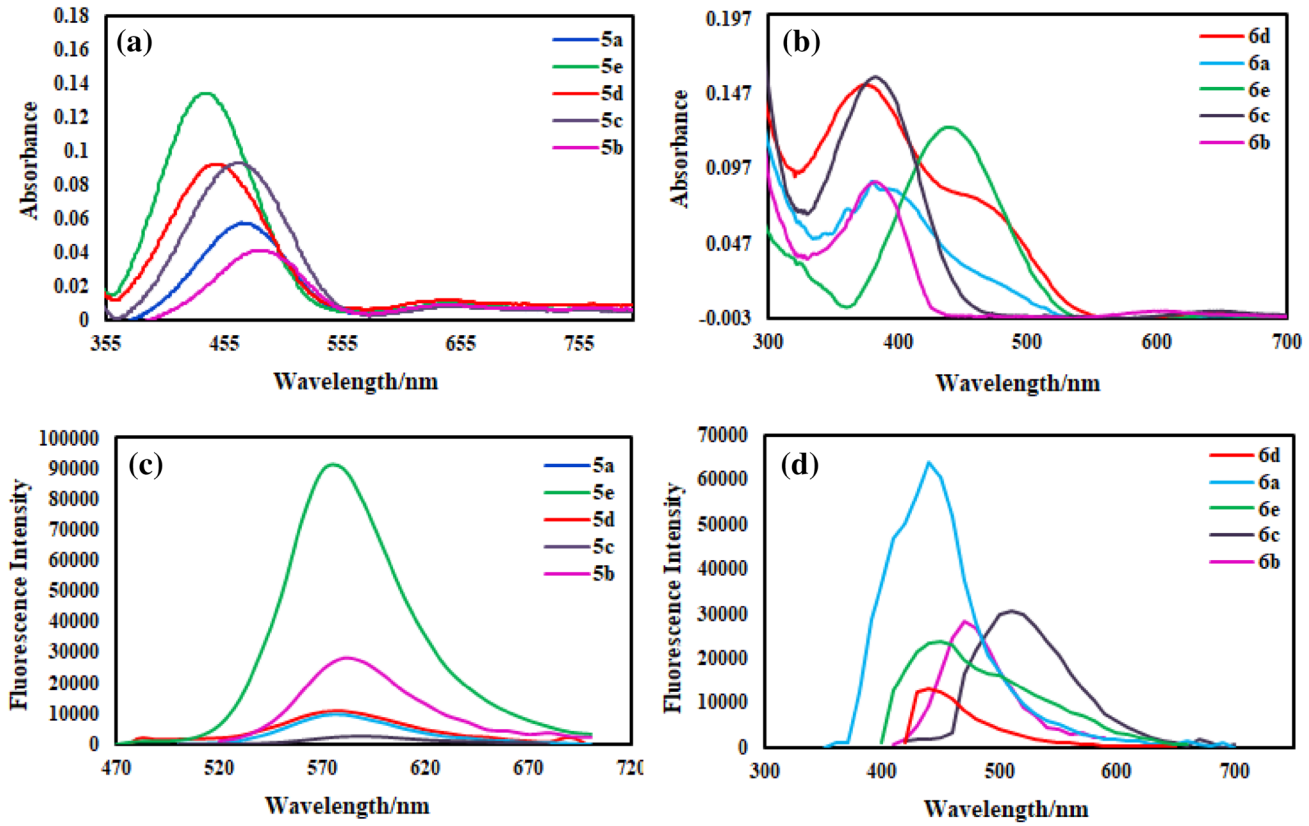


Fig. 3 Absorption (**a**, **b**) and fluorescence (**c**, **d**) spectra of **5**(**a**–**e**) and **6**(**a**–**e**)

Table 1 Fluorescent and UV–Vis parameters of products **5a**–**e** and **6a**–**e**

Entry	λ_{max} (nm)	λ_{em} (nm)	$\Delta\nu^a$ (cm^{-1})	Entry	λ_{max} (nm)	λ_{em} (nm)	$\Delta\nu^a$ (cm^{-1})
5a	475	580	3811	**6a**	402	440	2148
5b	491	580	3125	**6b**	387	470	4563
5c	465	590	4556	**6c**	388	520	6542
5d	453	580	4833	**6d**	378	440	3727
5d	443	580	5331	**6e**	442	450	402

[a]Stokes shift

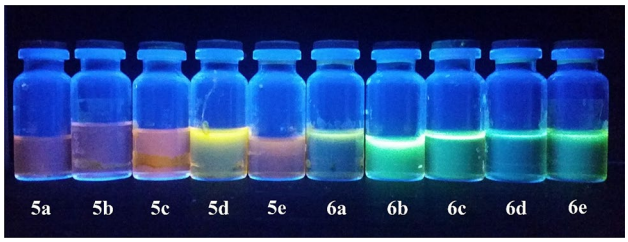


Fig. 4 Fluorescence emission photographs of synthesized compounds

Stokes shifts are calculated from the difference between emission and absorption wavelength of synthesized compounds, indicating low overlap between their absorption and emission spectra. Large Stokes shifts are one of the most desirable features for compounds with optical applications. Since in large Stokes shifts, the emitted photons separated from scattered excitation light and reabsorption of fluorescence photons by dye which reduce the efficiency do not happen.

Fluorescence emission photographs of compounds **5** and **6** are illustrated in Fig. 4. Fluorescent emission can be easily observed by naked eyes.

Conclusion

In summary, a convenient method has been developed for the synthesis of 3-[3-(4-amino)acryloyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one derivatives. In the first step, the reaction of 4-fluorobenzaldehyde with variety of amines in the presence of K_2CO_3 was described. In the next step, obtained amino-substituted aldehydes were reacted with DHA to produce new class of chalcones. These products have been successfully rearranged to pyran derivatives via Fries reaction. Optical properties of all synthesized compounds were studied using UV–Vis and fluorescence spectroscopy.

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